Quantitative constraints on mid- to shallow crustal processes using the zircon (U-Th)/He thermochronometer

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Abstract

Despite the potential of zircon He thermochronometry for constraining rock thermal histories, it remains less commonly exploited than the apatite He chronometer. In part this is due to the more challenging analytical techniques required to extract He, U and Th. Here we present a new method for the routine determination of zircon (U-Th)/He ages, and demonstrate how it can be used to constrain thermal histories, and to quantify cooling in different tectonic settings. We present zircon (U-Th)/He ages that place a firm upper limit on the extent of denudation-induced cooling (~ 3 km) on the SE Australian passive margin; a region where syn-rift apatite fission track and apatite (U-Th)/He ages have previously prevented quantitative constraint. We have also used the zircon (U-Th)/He thermochronometer to quantify the cooling of early Tertiary mafic plutons from Skye, Scotland, where the rate and timing of cooling cannot be determined using other thermochronometers.

The majority of studies that apply low temperature thermochronology to continental scale processes aim to resolve the rate, timing and distribution of uplift and denudation; typically in the context of orogenesis (e.g. Bigot-Cormier *et al.* 2000; Blythe *et al.* 2000), the evolution of passive rifted margins (e.g. Gallagher & Brown 1997; Lisker 2002), or the burial and exhumation of sedimentary basins (e.g. Duddy & Gleadow 1985). In these settings the combination of apatite fission track (AFT) and apatite (U-Th)/He (AHe) thermochronometry has provided temporal constraints on many shallow crustal processes (Persano *et al.* 2005; Spotila 2005; Stockli 2005). However to date, the quantitative constraint on the timing of cooling through higher temperatures has often been prevented by the poor understanding of crystal specific annealing behaviour of fission tracks in zircon (ZFT) (Hasebe *et al.* 1994; Yamada *et al.* 1995; Bernet & Garver 2005; Garver *et al.* 2005). The inability to accurately determine the timing of cooling between ~ 350ºC (the closure temperature of the K/Ar system in mica) and ~ 110ºC (AFT closure temperature) prevents the resolution of the timing and rate of shallow- and mid-crustal processes, and limits our understanding of the interplay between plate-scale tectonics and landscape evolution.

The zircon (U-Th)/He (ZHe) thermochronometer has a closure temperature of 170-190°C for typical cooling rates and crystal sizes (Reiners *et al.* 2002; Reiners *et al.* 2004), and has the potential to provide time-temperature constraints unavailable from existing thermochronometers. The common occurrence of zircon as an accessory phase in many igneous and metamorphic rocks, and its robustness in the geological record means that it can be applied to a wide range of studies. ZHe has previously been used to constrain the cooling of mid-crustal plutonic rocks (Reiners *et al.* 2002; Reiners & Spell 2002; Reiners *et al.* 2004; Kirstein *et al.* 2006), for dating volcanic tuff sequences (Reiners *et al.* 2002; Tagami *et al.* 2003; Reiners *et al.* 2004) and for determining sediment provenance using detrital zircon populations (Hourigan *et al.* 2003; Reiners *et al.* 2005). However, the application of the technique has been limited because of the analytical considerations. In particular, the time, effort and cost of U and Th extraction from zircon is considerably greater than from apatite (Tagami *et al.* 2003; Reiners 2005; Reiners & Nicolescu in press), and the prevailing analytical protocols are not without their complications (Reiners 2005; Reiners & Nicolescu in press). Here we present a technique that allows the routine determination of (U-Th)/He ages from single zircon crystals, and illustrate the strength of the new technique with two short studies.

Analytical technique

Zircons are hand-picked to be free from visible fluid/mineral inclusions, cracks and fractures using a stereoscopic microscope at x500 magnification. The crystal length, termination lengths, and orthogonal crystal widths, are determined using a graticule. Individual crystals are packed into 2.0 mm x 0.5 mm Pt-foil tubes that are crimped closed at each end. Helium extraction is now routinely performed using a diode laser (Foeken *et al.* 2006) but early experiments used a double-walled resistance furnace previously used for noble gas extraction at SUERC. For furnace extraction, Pt-foil tubes are wrapped in small Mo-foil envelopes to ease removal after helium extraction. For laser heating the Pt-foil packets are loaded directly into 3 mm deep pits a Cu laser pan. Complete helium extraction is achieved by 25 minutes heating at ~ 1200ºC. Laser helium blank levels (1.5 x 10^{-12} cc STP ^{4}He) are significantly lower than furnace blanks (1.4 x 10^{-11} cc STP ^{4}He). Helium re-extractions are performed routinely and are usually indistinguishable from the preceding hot blank, and generally less than 0.5% of the ^{4}He. Full details of gas extraction, clean up and He measurement are given in Foeken *et al.* (2006).

The Pt-foil packets are removed from the pan after He extraction. To prevent possible crystal loss and the incomplete extraction of volatilised U and Th that may have condensed onto the internal surface of the Pt-foil, the unopened degassed foil packets are placed in 0.35 ml Parrish-type Teflon© microcapsules with 30 µl of 11.2 M HCl and ~ 2.28 ng ^{230}Th and ~ 0.93 ng ^{235}U spikes dissolved in 300 µl 5% HNO_3. The sample solution is reduced by 50% on a hotplate at 80ºC and the microcapsules are sealed and refluxed overnight to completely dissolve the Pt-foil. The solutions are then evaporated to dryness, and rehydrated with 15 µl of 16 M HNO_3 and 180 µl of 27.6 M HF. Eight microcapsules are loaded into a 125 ml capacity Parr™ bomb with 180 µl 16 M HNO_3 and 9 ml 27.6 M HF. The assembled bomb was heated for 48 hours at 230 ± 1ºC in a thermostatically-controlled oven. To ensure that refractory fluoride salts are fully dissolved, the microcapsules are removed from the oven, evaporated to dryness and rehydrated with 195 µl 3 M HCl. The microcapsules are returned to the bomb with 9 ml 3 M HCl, and heated for a further 14 hours at 230ºC. This procedure is sufficient to dissolve the majority of zircons (Parrish 1987). The initial dissolution cycle can be extended if necessary.

The dissolution of the Pt-foil packets introduces ~ 200 µg Pt into the sample solution. The dissolved Pt forms $PtAr^{+}$ during ionisation in the plasma that generated peaks that interfere at several of the masses that are routinely measured for U and Th concentration

determinations. In particular, $^{198}Pt^{40}Ar^{+}$ (mass 238) and $^{195}Pt^{40}Ar^{+}$ (mass 235) restrict using the Pt-bearing solutions for U concentration measurement by conventional isotopic dilution techniques using quadrupole inductively-coupled plasma mass spectrometers (ICP-MS). For routine application the Pt is removed prior to analysis by anion exchange column chemistry. The purification of the sample and the reduction in the concentration of contaminant prevents $PtAr^{+}$ interference and removes the ~ 35% reduction in ICP-MS sensitivity that results from the high volume of dissolved species (Reiners & Nicolescu in press). The sample solutions are transferred from the microcapsules to 2 ml Teflon beakers. The solutions are evaporated to dryness then equilibrated with 1 ml 1.5 M HNO_3. Purification of the U and Th is achieved using Teflon columns loaded with 1 ml Eichrom TRU Resin (Blue). The columns are rinsed with 9 ml 0.2 M HCl and 9 ml 0.1 M HCl - 0.3 M HF, then pre-conditioned using 9 ml 1.5 M HNO_3 before the equilibrated sample solution is introduced. The Pt and other contaminants are removed with rinses of 12 ml 1.5 M HNO_3 and 2.5 ml 3 M HCl. Elution of U and Th is achieved using a rinse of 12 ml 0.1 M HCl & 0.3 M HF. The U- and Th-bearing elute is evaporated to dryness and equilibrated with 2 ml 5% HNO_3 and trace HF mixture prior to ICP-MS analysis. The microcapsules are cleaned by refluxing with 0.1 M HCl - 0.3 M HF on a hotplate at 130°C. 15 µl of 16 M HNO_3 and 180 µl of 27.6 M HF are then added to each microcapsule, and the microcapsules are loaded into the bomb and heated at 235°C for a further 48 hours. This procedure is sufficient, as blanks performed routinely yield levels of U and Th indistinguishable from background ICP-MS measurements.

U and Th analyses are performed on a VG PQ2plus ICP-MS. Isotopic fractionation is monitored using a certified U500 standard solution. U and Th measurements are replicated 5 times. The Pt-foil tubes used during this study contain measurable U and Th, that generates a procedural blank of 0.1067 ± 0.0149 ng U (n = 11) and 0.0997 ± 0.0110 ng Th (n = 11). Although analysis of single crystals is possible, until the U and Th content of a sample is established, aliquots of 2 - 3 crystals are preferred, in order to ensure that the uncertainty in the U and Th blank has a minimal effect on the measured U and Th concentrations and the calculated ZHe age.

Zircon (U-Th)/He age standards

Zircon from the Fish Canyon Tuff (FCT) has been adopted as the ZHe age standard mineral (Reiners *et al.* 2002; Tagami *et al.* 2003; Reiners 2005). Unlike the Durango apatite standard, (U-Th)/He ages of FCT zircon are determined on complete crystals and

therefore all ages require correction for the recoil loss of ^{4}He at the crystal boundaries (Farley 2002). In this study, the recoil correction is based on measured grain dimensions and uses the equations developed by Hourigan *et al.* (2005). The average (U-Th)/He age of the 16 FCT zircon aliquots analysed as part of this study (27.6 ± 3.3 Ma; Table 1) is indistinguishable from the He ages of 28.3 ± 2.6 Ma (n = 83) reported by Reiners (2005), and the average age of 127 analyses from all laboratories (28.3 ± 3.1 Ma, Tagami *et al.* 2003; Reiners 2005, Pik, pers. com.) (Figure 1).

The age reproducibility of this standard (± 11%) is significantly poorer than the analytical precision (typically ± 2%, Dobson 2006; Reiners & Nicolescu in press), and the He age reproducibility of the Durango apatite standard (typically ± 6 - 8%, Farley 2002; Boyce & Hodges 2005). This is thought to be because of heterogeneous and variable U and Th distributions within the zircons, which can exhibit up to a factor of 20 change in the concentration gradients in the outer 20 µm of some crystals (Dobson 2006). The uncertainty in the age of unknown samples is generally calculated from the 2σ reproducibility of relevant mineral standards (e.g. Reiners 2005). Using the FCT zircon as an age standard limits the precision with which dating can be performed, and the variable zonation of U and Th in FCT zircon also prevents a true estimation of analytical precision (Dobson 2006).

The Muck Tuff (MT) is a sequence of zircon-bearing crystal lithic tuffs that are preserved on the island of Muck, western Scotland. These tuffs mark the earliest Palaeogene volcanism on the European Atlantic margin (Saunders *et al.* 1997), and field relationships indicate it has been within 500 m of the surface since ~ 58.7 Ma (Chambers *et al.* 2005). Five single zircon aliquots from Camas Mor, Muck, have an average He age of 58.8 ± 3.5 Ma (Table 1). This is within error of the zircon U/Pb age (61.15 ± 0.25 Ma; Chambers *et al.* 2005) and sanidine ^{40}Ar/^{39}Ar age (62.8 ± 0.6 Ma; Pearson *et al.* 1996 to to 60.45 ± 0.03 Ma; Chambers *et al.* 2005) obtained from this sample, implying that the Muck Tuff cooled to < 170°C rapidly after eruption and experienced no reheating. The age reproducibility of the Muck Tuff is significantly better (± ~ 6%) than that determined for the Fish Canyon Tuff zircons (± ~ 11%), and is approximately the same as reported for the Durango apatite standard. The improved reproducibility of the MT may be due to less inter-crystal variation of U- and Th-zonation, therefore improving the accuracy of the alpha-recoil correction. We suggest that the age reproducibility of the MT zircons reflects better the true precision with which ZHe ages can be determined, and that it may be a more appropriate age standard than FCT zircons. Further work constraining the

effect of variable U-Th-zonation in crystal populations on the alpha-recoil correction is ongoing (Dobson 2006, Dobson *et al*. in prep).

Application of zircon (U-Th)/He thermochronology

Constraining exhumation at passive margins

AFT thermochronology is sensitive to cooling from ~ 110 - 70ºC (Laslett *et al.* 1987; Ketcham *et al.* 1999). This corresponds to the removal of a crustal section of less than 4 km when geothermal gradients are 25 - 30ºC km^{-1}. The apatite (U-Th)/He thermochronometer is sensitive to cooling from ~ 75 - 35ºC (House *et al.* 1999; Farley 2000), and can be used to determine the timing of removal of 1 - 2 km of crust. Combining the AHe and AFT thermochronometers in samples from the southeast Australian and the Eritrean high elevation passive margins has demonstrated that continental break up-driven denudation varied systematically across both margins. Denudation decreases from a maximum at the present coastline, where syn-rift AFT and AHe ages are similar, to the continental interior, where ages may be 100's Myr older (Persano *et al.* 2002; Balestrieri *et al.* 2005; Persano *et al.* 2005). The syn-rift AFT ages at the coast prevents a precise determination of the amount of denudation, and a higher temperature thermochronometer is necessary to in order to (i) constrain the maximum amount of break up-driven denudation at the rifted margin, and (ii) determine the volume of sediments delivered to the offshore basins. Constraining the maximum amount of breakup-driven denudation experienced by a continental margin has important implications for the understanding of the flexural properties of the crust that allow erosion-driven isostatic rebound to occur. Numerical models of landscape evolution at the eastern Australian passive margin indicate that for typical values of crustal elastic thickness (Te = 10 - 15 km), denudation at the coast could not have exceeded 2 km (Brown & Van der Beek, 2004). This implies that the geothermal gradient at the time of rifting was at least 60°C km^{-1}. If the geothermal gradient has remained constant at 25°C km^{-1} since before breakup, the minimum amount of denudation derived from the syn-rift AFT ages (3 to 4 km) can only be accommodated by an elastic thickness of 8 km. Although this is an acceptable value, it is at the low end of the range determined for continental crust (Braun & Van der Beek 2004). If the amount of syn-rift denudation was significantly greater, i.e. if the samples now at the surface were at more then 110°C at the onset of continental break up, a constant geothermal gradient of 25°C km^{-1} would require unrealistically low values of Te. If faulting can be discounted, cooling from significantly

more than 110°C implies a significantly higher syn-rift geothermal gradient. An accurate estimation of the maximum amount of cooling during rifting has the potential to constrain this palaeogeothermal gradient.

Along the southeastern coast of Australia AFT and AHe ages are indistinguishable from each other, and to the age of rifting (Persano *et al*. 2002; 2005) (sea floor spreading began at c. 85 Ma; Weissel & Hayes, 1977). In a preliminary study we have determined zircon He ages from the Bega granite (crystallisation age of ~ 400 Ma; Chappell & Stevens 1988; Williams 2001) within 5 km of the coast (99-OZ-12; Table 2) in order to constrain the maximum amount of denudation at the south-eastern Australian passive margin. This sample previously yielded an AFT age of 135 ± 5 Ma and an AHe of 90 ± 9 Ma (Persano *et al.* 2005), and on the basis of remagnetisation of pyrrhotite Dunlop *et al.* (2000) have argued that pre-breakup temperatures were 165 ± 30°C. Two aliquots of two euhedral zircon crystals yield reproducible recoil-corrected ZHe ages of 286 & 298 Ma respectively (Table 1). These are almost 200 million years older than breakup. By combining the zircon He ages with the existing AFT thermochronology it is possible to constrain the pre-breakup thermal history of the margin and determine the amount of cooling during the isostatic uplift after breakup (Persano *et al.* 2005). In Figure 2 we show the He ages (uncorrected for alpha-recoil) predicted for a range of thermal histories for zircons with the same surface area-to-volume ratio as the analysed crystals. The He ages vary from 70 to 280 Ma depending on the cooling rate (Figure 2B). Assuming the relatively simple thermal histories modelled here, the measured ZHe ages are consistent with a relatively rapid post-crystallisation cooling (~ 7°C Myr^{-1}) followed by a period of slower cooling (~ 0.1°C Myr^{-1}) until the time of break up, when the cooling rate dramatically increased (Persano *et al.* 2005). High rates of cooling in the early Devonian are consistent with typical plutonic cooling profiles and indicate that the granite cooled to ~ 200°C in less than 50 Myr. This suggests that this pluton was intruded at relatively shallow depth (between about 5 and 8 km for palaeogeothermal gradients of 20-35°C km^{-1}), or was exhumed to this depth immediately after intrusion. A long period of slow cooling is consistent with the old apatite fission track (250 - 350 Ma; Dumitru *et al.* 1991; Gleadow, 2000; Persano *et al.* 2005) and He ages (200 - 250 Ma; Persano *et al.* 2005) and mixed fission track length distribution found where the south east Australian highlands were not subjected to break up-related denudation (Persano *et al.* 2005).

In order to constrain the amount of breakup denudation we need to determine the temperature of sample 99-OZ-12 at ~ 100 Ma. To achieve this we have calculated the He age of zircons for a suite of thermal histories (Figure 3) that span the range predicted by

preliminary models. These thermal histories include a period of rapid cooling from >350°C, and the samples cool to 200 - 170°C at 370 Ma, followed by variably slow cooling monotonic until 100 Ma. The predicted ZHe ages are indistinguishable from the measured age if the sample cooled to 100°C (for slow cooling starting at 200°C) and 125°C (for slow cooling starting at 170°C) at ~ 100 Ma (Figure 3). These results indicate that the rocks now at the coast were close to, or slightly beyond, the base of the apatite partial annealing zone at the onset of break up. Consequently the amount of denudation derived from the AFT-AHe data (2 to 4 km, depending on the geothermal gradient) is close to the maximum amount experienced by the margin. The ZHe ages are inconsistent with the suggestion that remagnetisation indicates break up temperatures of 165 ± 30°C (Dunlop *et al.* 2000). Higher temperatures were either very localised or were short-lived and therefore did not affect the He diffusion in zircon.

Constraining the cooling of plutonic systems

While the cooling history of acid igneous rocks can generally be constrained using a number of mineral thermochronometers, the cooling history of mafic and ultra-mafic rocks tends to be more difficult to extract because of a paucity of mineral phases suitable for radiometric dating. This generally limits the thermal constraint to crystallisation ages determined from U/Pb analysis of zircon. Poor constraints on the thermal history prevent determination of the depth of emplacement, the timescale of hydrothermal activity and associated mineralization, and establishing accurately the duration of magmatic activity. Even for plutonic units where the application of $^{40}Ar/^{39}Ar$ and FT thermochronology has allowed the partial constraint on the cooling history, the ZHe thermochronometer can provide additional and more specific time-temperature constraint (Reiners & Spell 2002; Reiners *et al.* 2004).

The Palaeogene extrusive and intrusive volcanic sequences of the European North Atlantic margin were generated in response to the impact of the proto Iceland plume (Saunders *et al.* 1997). The Hebridean Igneous Province (HIP) (Figure 4) is one of the earliest igneous provinces on the European rift flank, and lies along the west coast of Scotland. The HIP is characterised by three fissure-fed basaltic lava fields and four plutonic complexes. These plutonic complexes represent the root zones of Palaeogene volcanoes (Bell & Williamson 2002) and are thought to have been emplaced at depths of 2 - 3 km (Holness 1999; Bell & Williamson 2002). Post-magmatic denudation has removed much of the basaltic sequence, and the timing and volume of material removed during this denudation episode is poorly constrained. Recent radiometric dating has

provided high precision U-Pb (zircon) and Ar/Ar (biotite and sanidine) ages for several of the intrusive units across the HIP, but constraint of the plutonic cooling through lower temperatures is limited to ZFT from the plutonic units of the Skye plutonic complex (Lewis *et al.* 1992). These data suggest that there was prolonged heat flow through the shallow level plutonic complex (Lewis *et al.* 1992). The source of this heat remains unidentified, and continued heat flow is inconsistent with field evidence for rapid syn-magmatic denudation (Brown 2003), and short lived magmatic activity (Bell & Williamson 2002). No low temperature constraints have been placed on the plutonic cooling of the other plutonic complexes.

In order to constrain the cooling of the plutonic complex on the Isle of Mull (Figure 4), zircon He thermochronometry was performed on euhedral zircons from two samples. ML5 is a gabbro which from field relationships was emplaced during the main phase of intrusion (58.3 Ma, U/Pb; Hamilton in Emeleus & Bell 2006); whereas ML3 is from the youngest intrusion in the complex, the Loch Ba Felsite (58.5 Ma, U/Pb; Hamilton in Emeleus & Bell 2006). The ZHe ages from both samples are indistinguishable, with an average age of 58.1 ± 6.6 Ma (Table 2), and shows that the Mull plutonic complex cooled to below ~ 170ºC very rapidly (at in excess of 200°C Myr^{-1}), immediately after intrusion (Figure 5). This is in sharp contrast to the ZFT data from the Skye plutonic complex, which suggests that temperatures remained at ~ 250°C until ~ 47 Ma (Lewis *et al.* 1992). The cooling of the Mull plutonic complex is consistent with the short period of intrusion suggested from the radiometric crystallisation ages, and field evidence for rapid unroofing immediately after the cessation of magmatic activity (Emeleus & Bell 2006). A more complete investigation of the cooling of the HIP will be presented elsewhere.

Concluding thoughts

We have developed a methodology for the determination of zircon He ages that enables routine age determination without the possibility of crystal loss, parent-element loss, mass interference or loss of sensitivity during U and Th measurement. The application of this methodology is limited only by the time required for the anion exchange chemistry, and by U and Th blank in the Pt-foils. The technical developments presented here have allowed the identification of are several issues that require further investigation. Most important is the need to accurately correct for He-recoil loss when crystals exhibit U- and Th-zonation, and to fully understand the effects of zonation on helium diffusion. However, we have shown that the application of the ZHe thermochronometer can provide

constraints on the rates, timings, and amounts of rock cooling in the mid- to shallow-crust that are generally unavailable with other techniques.

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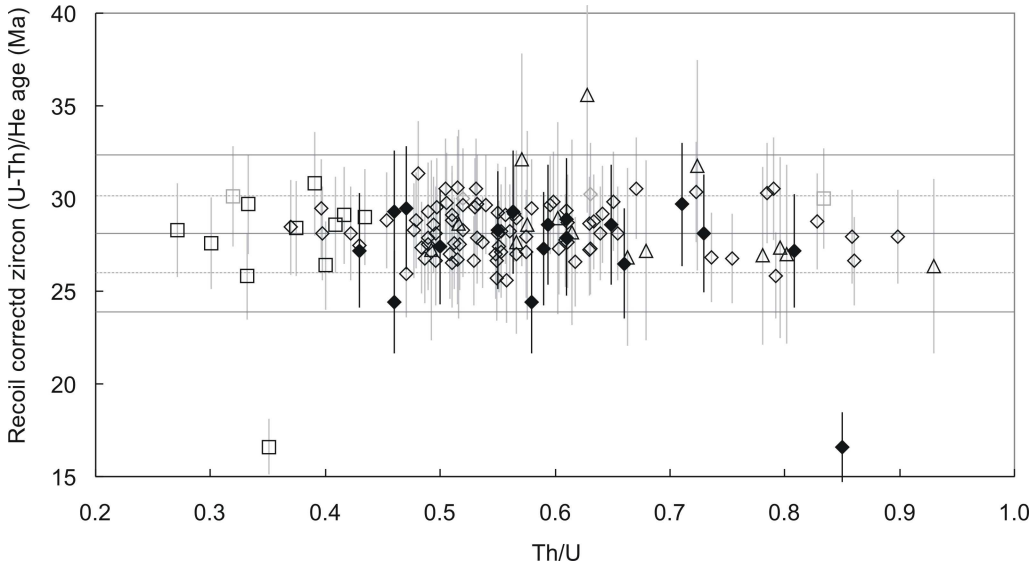

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442 Fig. 1. The zircon (U-Th)/He ages of the Fish Canyon Tuff. Data from all laboratories
443 routinely making ZHe age determinations are shown: open diamonds - Reiners (2005),
444 open squares - Tagami *et al.* (2003), open triangles - Pik (pers. comm)., filled diamonds -
445 this study. All error bars are 2σ. The two ZHe ages younger than 20 Ma are not included
446 in the average age calculation. These samples may be affected by an extreme form of U
447 and Th zonation (Tagami *et al.* 2003; Dobson 2006). The average age of the FCT zircons
448 is 28.3 ± 3.1 Ma (2σ, n = 127).

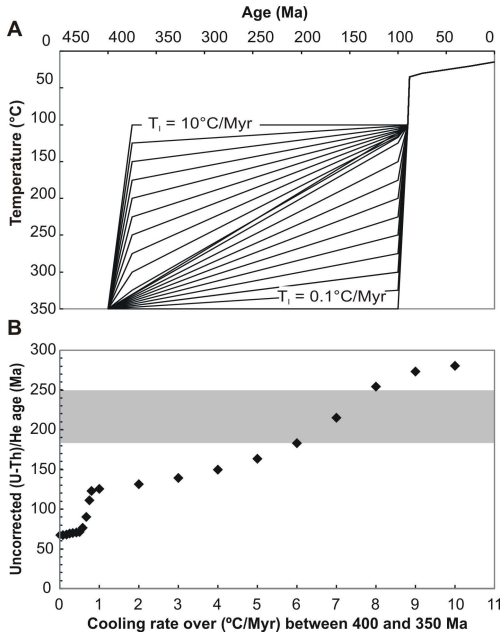

Fig. 2. (A) The possible thermal histories for the coastal samples from SE Australia. The time-temperature constraint at ~ 400 Ma is derived from the emplacement age of the Bega batholith (Chappell & Stevens 1988), 90 Ma is the latest time at which the sample could have passed through 100°C (Persano *et al.* 2005). These thermal histories were used to predict the zircon (U-Th)/He ages shown in (B). (B) The uncorrected zircon He ages predicted from the thermal histories in A plotted as a function of the initial cooling rate from 400 Ma. Zircon He ages were predicted using DECOMP (Meesters & Dunai 2002) using the He diffusion parameters in zircon, D_0 = 0.46 cm s^{-1} and E_a = 40.4 kcal mol^{-1} (Reiners *et al.* 2004) and a stopping distance of 17 μm (Hourigan *et al.* 2005). "Uncorrected" ZHe ages are used because these are the form of the data output by DECOMP and previous studies have shown that applying an alpha-recoil correction is unjustified unless cooling is rapid (Meesters & Dunai 2002). The grey region represents the "uncorrected" measured He age 217 Ma with a ± 15 % (± 33 Myr) uncertainty, as calculated from the reproducibility of the uncorrected He ages of the FCT (Table 1). A cooling rate of between 6 and 8°C/Myr best fits the measured uncorrected ages, this means that the sample was between 200°C and 170°C at 370 Ma.

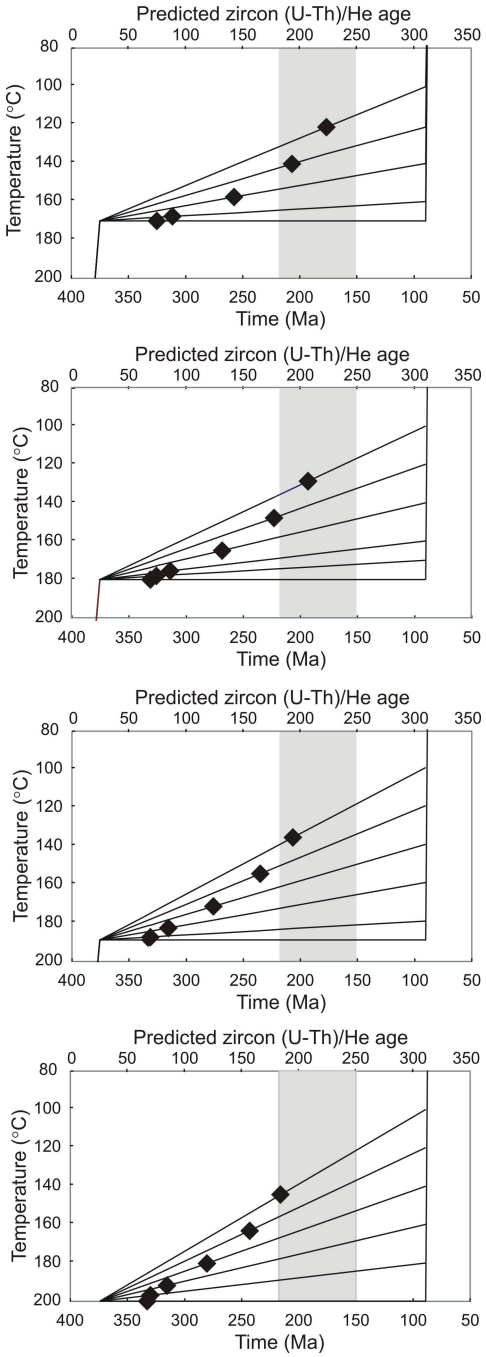

Fig. 3. Modelled time-temperature paths of the coastal samples at the onset of rifting where cooling starts at 370 Ma at 170°C (top panel) to 200°C (bottom panel), using the constraints provided by Figure 2B and the latest time at which the sample could have passed through 100°C (Persano *et al.* 2005). The DECOMP derived ZHe ages for each thermal history are as black diamonds, on the corresponding time-temperature path. The acceptable time-temperature paths are those where the predicted ages fall within the shaded region, which represents the uncorrected measured ZHe age of the coastal sample 99-OZ-12 (as on Fig 2B). The plots show that this sample cannot have been at temperatures in excess of 125°C at the onset of rifting (100 to 90 Ma).

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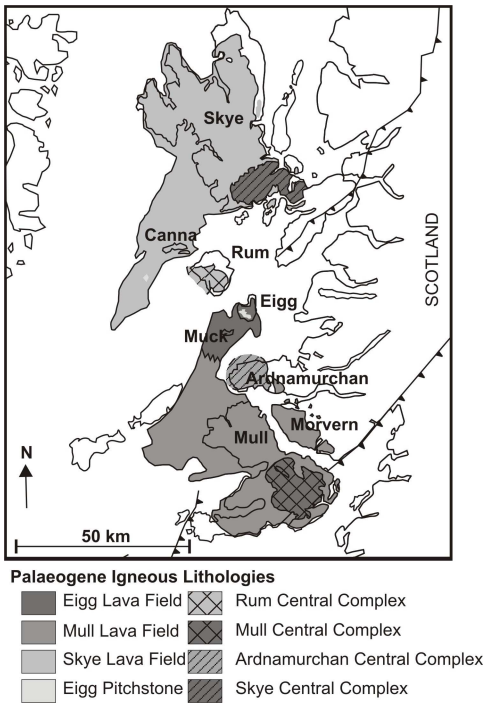

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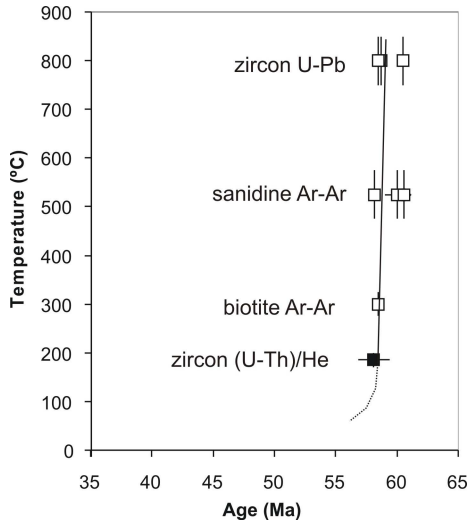
478 Fig. 4. A map of the Hebridean Igneous Province, NW Scotland [modified after Emeleus
479 & Bell 2006].



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481 Fig. 5. The U/Pb (in Emeleus & Bell 2006), Ar/Ar (Chambers & Pringle 2001) and zircon
482 (U-Th)/He ages determined on plutons from the Mull plutonic complex.